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Synthesis mechanisms of poly(oxybenzoate) liquid crystal polymers

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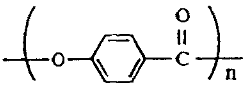
Summary

Evidence is presented for the growth of bilayered lamellae during the polymerization of *p*-acetoxybenzoic acid to form uniform thickness poly(p-oxybenzoate) lamellar crystals. Fracturing one preparation of these crystals lead to the formation of fibers connecting the fracture faces, reminiscent of those formed during fracture of folded chain flexible polymer single crystals. The results raise questions concerning previously proposed polymerization - crystal growth mechanisms.

Introduction

Poly(oxybenzoate)*  (POBA) and related copolymer "rigid rod" liquid crystal polymers (LCPs) are often polymerized by condensation polymerization in a high temperature monomer solvent. Two related mechanisms of polymerization are generally accepted, depending on the concentration (1). In both cases the initial steps involve the formation of short chain oligomers which crystallize out of solution at a DP of 10 or less to form paraffin-like, i.e. extended chain, lamellar crystals. In dilute solutions further chain growth was suggested to occur by polymerization on the two "end" surfaces, both of which remain active. With more concentrated solutions multilayered lamellar crystals grow from solution, the oligomers adding presumably more or less end to end before joining by polymerization as well as adding onto the lateral surfaces.. If the polymerization-precipitation temperature is below the crystal-liquid crystal transition ($T_{c\text{-}lc}$) it was suggested further polymerization (chain growth) does not occur, the ends being unable to approach each other when "locked" in the crystal lattice; if axial translation is possible polymerization may proceed, the end result, as in the first case, being lamellae in which the chain length equals the lamella thickness. Although the monomers and

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* Also described as poly(hydroxybenzoic acid) or poly(acetoxybenzoic acid) depending on the monomer used.

polymers are polar, i.e. have a direction to their backbone, there is no evidence as to whether the chains are parallel, antiparallel or randomly directed in the resulting crystals. In addition, although chain folding has been suggested to occur in the as-polymerized lamellae (1-3), there has neither been evidence nor a plausible mechanism presented for it. It would seem to require endlinking of neighboring chains, a feature which would require both an antiparallel packing of neighboring chains and a more than expected flexibility and mobility, even if the link is made by the addition of an additional, hairpin shaped oligomer rather than reaction between two neighboring chain ends.

As part of our research on the morphology, structure and transitions of "rigid rod" liquid crystal polymers we have been polymerizing POBA between glass slides immersed in the polymerization medium, to produce individual polymer crystals suitable for electron diffraction. SEM observation of the corresponding POBA samples, as polymerized in the bulk solution, have both raised significant questions concerning the "accepted" polymerization mechanics and some answers. Two of the more interesting observations are described here; further details are in a forthcoming paper (4).

Experimental

Para-acetoxybenzoic acid was obtained from Aldrich Chemical Co. The samples were polymerized in Therminol 66* at a 1/5 (wt/vol) concentration in an Ehrlenmeyer flask, in a heating mantel, with a condensor for the acetic acid. Following polymerization the samples were washed overnight in acetone in a Soxhlet extractor to remove residual monomer and low molecular weight materials. Observation was in an Hitachi S570 SEM after coating with gold.

Results and Discussion

Figures 1 and 2 are scanning electron micrographs of POBA polymerized in a concentrated (20% wt/vol) Therminol 66 solution at 300°C for 1.5 hours; the sample in Fig. 2 was ultrasonically treated in an attempt to disperse the lamellae. The lamellae at the top and lower right of Fig. 2 were fractured, the fracture faces being to the right of the small headed arrows; they resemble those produced by the fracture of pressure crystallized extended chain polyethylene (5). With a $T_{c\text{-}Ic}$ of 326°C, corresponding supposedly to a chain length of ca. 600A ($DP_n \sim 100$) (6), and considering the concentration, it is likely these crystals grew by the second mechanism (oligomer crystallization) but, because of the low polymerization temperature, did not fully endlink within the crystals.

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* Trademark of Monsanto Co. for a heat transfer fluid consisting of bi- and triphenyls.

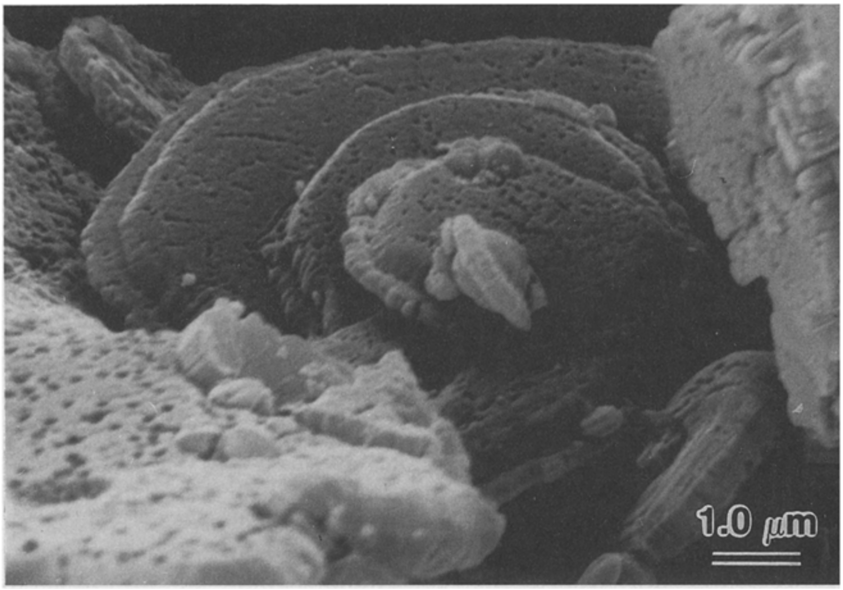

Fig. 1. POBA as-polymerized bilayer lamellae. X-ray shows this sample to be predominantly Phase I.

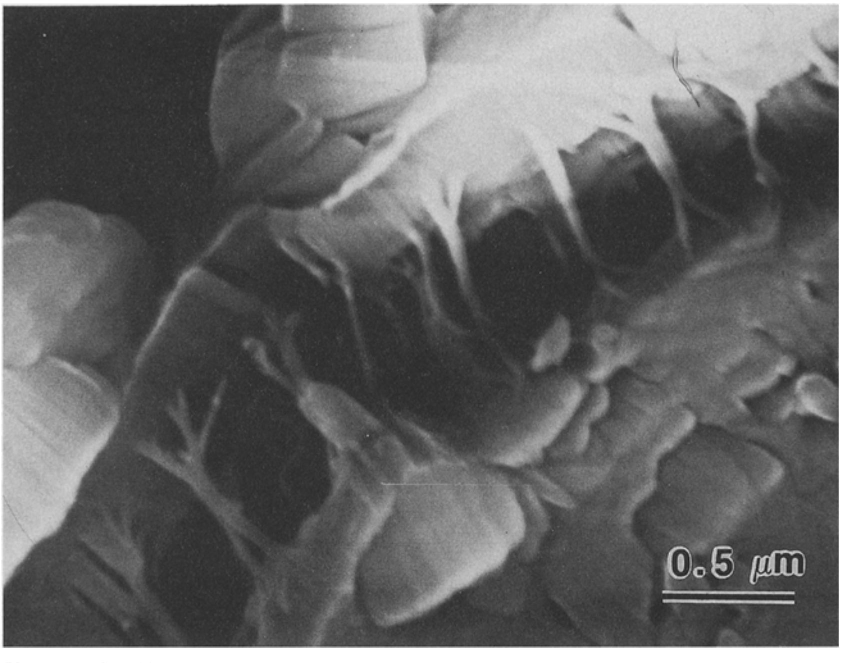

Fig. 2. Ultrasonically treated samples as in Fig. 1. The bilayered structure of the lamellae is clearly seen on the fracture faces to the right of the small headed arrows. The large headed arrow indicates fracture through a monolayer domain.

Clearly the lamellae in the preparation are bilayers of near uniform thickness except at the very edge where they taper sharply, and with little or no adhesion at their interface; there has been no endlinking reaction at the interface over most of the fracture face even if it has occurred within each layer. The bilayer structure and lack of reaction at the interface implies that the initial crystal nucleus was bilayered also, with the oligomers being parallel in each layer, but in opposite directions; they thus can not endlink regardless of the temperature. In the upper lamella of Fig. 2 (large headed arrow) the bilayers appear coherent; perhaps in this portion of this crystal a random or antiparallel chain direction packing occurred permitting endlinking across the interface. The uniformity in thickness (reasonably so from lamella to lamella also) and the shape of the growth faces of the "sheets" suggests the growth in thickness of the layers is much more restricted than the lateral growth. The porous nature (seen also in the untreated samples, as in Fig. 1) is also noted. For either of the proposed mechanisms the center of the crystal, having grown for a longer time, should be thicker than the edges; the whole lamelia should taper unless the thickness of the crystal (and maximum length of the molecule) is determined by e.g., the temperature of polymerization.

Even more unexpected in terms of the proposed mechanisms of polymerization and despite the evidence-less suggestions of folding, was our observation (Fig. 3) of "long" fibrils being torn off the fracture faces of ultrasonically treated lamellae of another sample grown from the same concentration, but polymerized for 5 hrs at a somewhat higher temperature (300-350°C). Similar fibrils were also seen in the ultrasonically treated sample used for Fig. 2. The lamellae in this sample are only slightly thicker than the total bilayer thickness of the lamellae in Fig. 1 and 2, despite the higher temperature and longer time of polymerization. The fibrils, on the other hand, are at least twice as long as the lamella thickness and are being stripped off of the fracture face. This is in contrast to the fibrils that split off of the fracture faces of fractured extended chain polyethylene for which the length is equal to the lamella thickness (5). Clearly some kind of linking of neighboring molecules is occurring on the surfaces of the lamellae, resembling folding. Not clear, however, is whether adjacent molecules are linked, as in adjacent re-entry folding of flexible polymer molecules or whether the whole fibril bends back on itself. Visible in the prints, but probably not in the reproduction, are small white bumps at positions that appear to correspond to the original lamella surface.

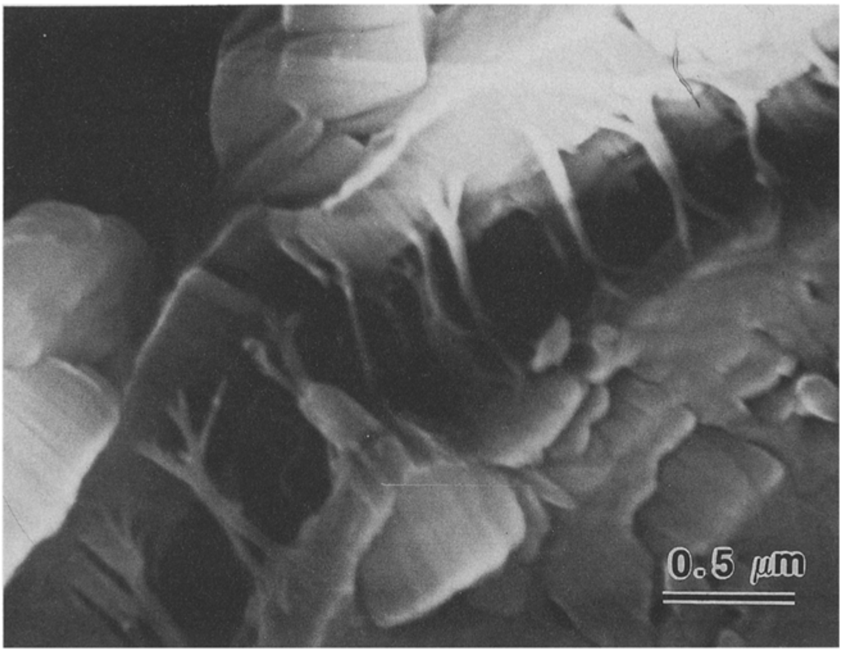

Fig. 3. Ultrasonically broken POBA lamellae with interconnecting fibrils.

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